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Synthesis of Mononuclear Paramagnetic Zirconium(III) Derivatives

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The coordination chemistry of the heavier members of group 4, namely Zr and Hf, is dominated by the +4 formal oxidation state.[1] This is in stark contrast to the lightest member of this group, Ti, for which the trivalent state, Ti(III), is almost as common as Ti(IV).[1] Attempts to prepare Zr(III) derivatives have normally resulted in the formation of diamagnetic, dinuclear complexes.[2-15] While there are reports that describe the observation of transient Zr(III) species as intermediates,[16-27] there are only three mononuclear Zr(III) complexes, $(\eta^5\text{-}C_5Me_5)Zr(\eta^8\text{-}C_8H_8)$,[28] $(\eta^5\text{-}1,3\text{-}C_5H_3Bu^t{}_2)_2ZrCl$,[29] and $Bu_4N[\{(\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}_2ZrCl_2]$,[15] that have been structurally characterized so far. These last examples illustrate that with sufficiently sterically demanding ligands, the tendency of the Zr(III) state to dimerize and possibly disproportionate[27] can be avoided. In this report we present our recent results on the preparation of a series of mononuclear Zr(III) complexes that also incorporate hydrocarbyl and hydride ligands. These paramagnetic Zr(III) derivatives provide the first opportunity to examine the reactivity of Zr–C and Zr–H bonds in d^1 complexes.

We have previously shown that reduction of the Zr(IV) complex $Zr(\eta^5\text{-}C_5H_5)Cl_2[N(SiMe_2CH_2PPr^i{}_2)_2]$ (**1**) with excess Na/Hg under N_2 leads to the formation of the dinuclear dinitrogen complex $\{[(Pr^i{}_2PCH_2SiMe_2)_2N]Zr(\eta^5\text{-}C_5H_5)\}_2(\mu\text{-}N_2)$.[30] During this process, there is a color change from yellow to deep green, which persists for hours, followed by a slow change to deep brown due to the color of the dinuclear dinitrogen derivative. By controlling reaction times, we have been able to intercept the intermediate in high yield as dark green crystals of $Zr(\eta^5\text{-}C_5H_5)Cl[N(SiMe_2CH_2PPr^i{}_2)_2]$ (**2**).[31] The ^1H NMR spectrum of **2** is consistent with it being a paramagnetic system, since only broad resonances are observed and no signals are observed in the $^{31}P\{^1H\}$ NMR spectrum; moreover, the ESR spectrum shows a binomial triplet at $g = 1.955$ with coupling to phosphorus-31 ($a(^{31}P) = 20.1$ G) and satellites due to one magnetically dilute Zr nucleus ($a = 37.2$ G, ^{91}Zr, 11.23%, $I = {}^5/_2$).

Metathesis reactions of the mononuclear Zr(III) complex **2** proceed smoothly; thus, reaction of **2** with Me_3SiCH_2Li and MeMgBr generates the corresponding alkyl derivatives $Zr(\eta^5\text{-}C_5H_5)CH_2SiMe_3[N(SiMe_2CH_2PPr^i{}_2)_2]$ (**3**) and $Zr(\eta^5\text{-}C_5H_5)Me[N(SiMe_2CH_2PPr^i{}_2)_2]$ (**4**), respectively.[31] Once again, the solution spectroscopic data are consistent with these complexes being mononuclear zirconium(III) alkyl complexes; thus, the ESR spectra of **3** (Figure 1) and **4** show a pattern consistent with coupling to two phosphorus nuclei with additional coupling to the α-hydrogens and the amide nitrogen, and the ^1H NMR spectra display only broad peaks. Solution magnetic studies of **3** give a value of one unpaired electron ($\mu_{eff} = 1.73\ \mu_B$ using the Evans method). The single-crystal X-ray structure of the (trimethylsilyl)methyl derivative **3** confirms that this complex is mononuclear in the solid state as well (Figure 1). The geometry can be described as a distorted trigonal bipyramid with the phosphine donors occupying the axial sites; the Zr–C bond length of 2.337(5) Å and Zr–C–Si bond angle of 130.0(3)° are within the observed range of Zr(IV) complexes containing bulky alkyl groups.[32-35] The metathesis reaction of the starting Zr(III) chloride can also be extended to the phenyl derivative $Zr(\eta^5\text{-}C_5H_5)Ph[N(SiMe_2CH_2PPr^i{}_2)_2]$ (**5**) by reaction with PhLi and to the tetrahydroborate complex $Zr(\eta^5\text{-}C_5H_5)BH_4[N(SiMe_2CH_2PPr^i{}_2)_2]$ (**6**) by reaction with $LiBH_4$; the X-ray structures of these derivatives have also been determined, and their overall geometries and bond lengths are comparable to those of the (trimethylsilyl)methyl derivative **3**. These are the first X-ray analyses of mononuclear zirconium(III) complexes containing simple hydrocarbyl ligands[36] or a BH_4^- unit.

Reaction of the Zr(III) alkyl complexes with H_2 (1 atm) proceeds smoothly at room temperature over a period of 10–12 h (monitored by ESR) to generate the mononuclear Zr(III) hydride complex $Zr(\eta^5\text{-}C_5H_5)H[N(SiMe_2CH_2PPr^i{}_2)_2]$ (**7**); the

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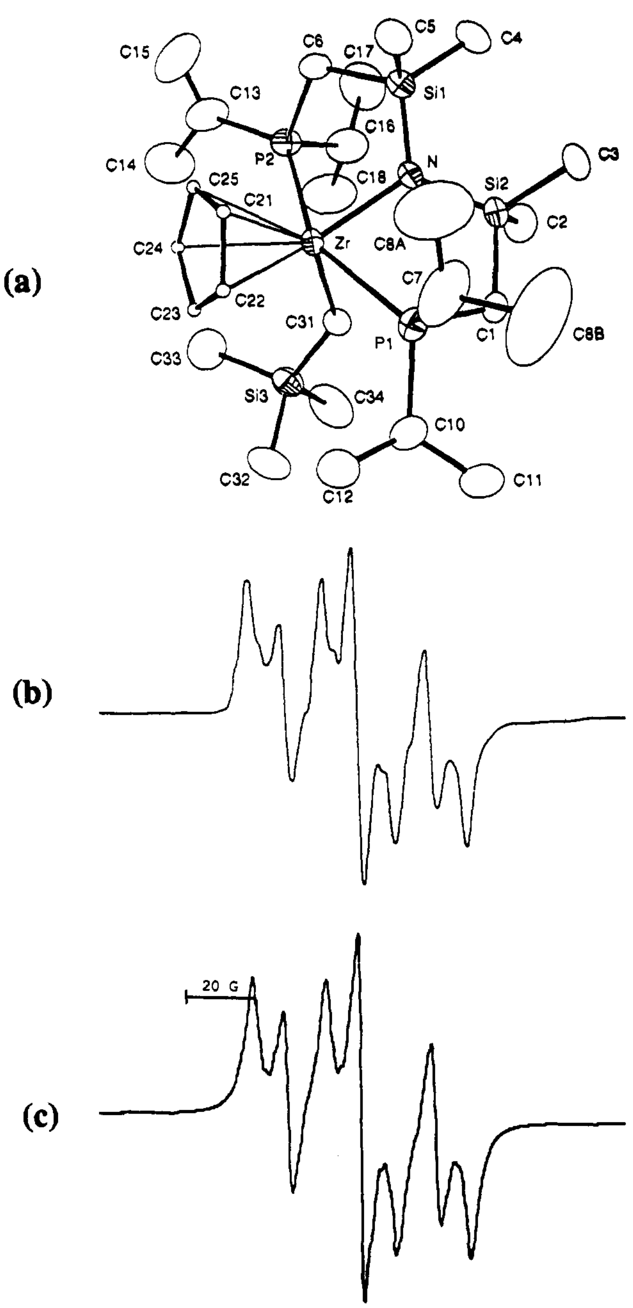
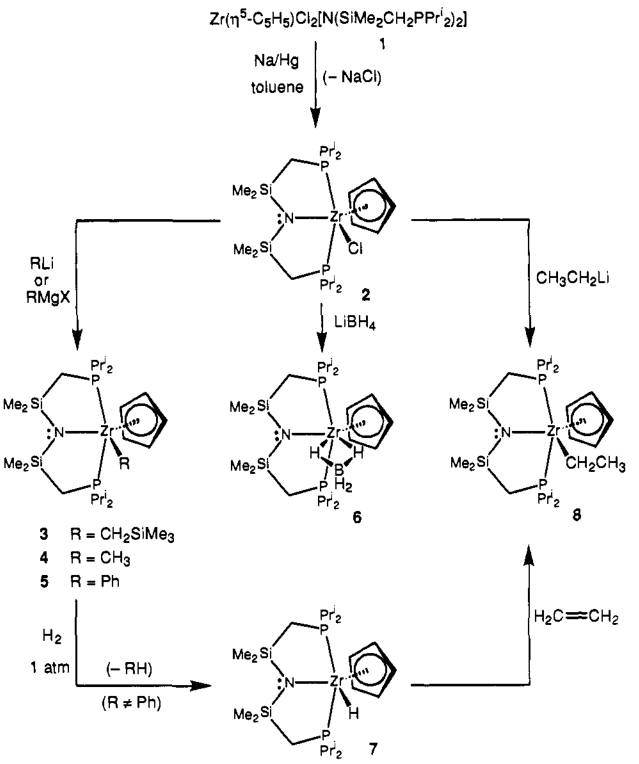


Figure 1. (a) Molecular structure and numbering scheme for Zr(η^5-C$_5$H$_5$)CH$_2$SiMe$_3$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] (**3**). Selected bond lengths (Å) and bond angles (deg): Zr–P1, 2.7923(16); Zr–P2, 2.8563(17); Zr–N, 2.216(4); Zr–Cp(cent), 2.2165(5); Zr–C31, 2.337(5); C31–Si3, 1.843(5); P1–Zr–P2, 151.17(5); P1–Zr–N, 77.83(11); P2–Zr–N, 94.39(14); N–Zr–Cp(cent), 139.47(10); C31–Zr–Cp(cent), 118.05(13); Zr–C31–Si3, 134.0(3). (b) Observed ESR spectrum of **3** (toluene, room temperature). (c) Simulated ESR spectrum of **3** using the following parameters: $a(^{31}\mathrm{P}) = 21.4$ G, 2 P; $a(^{1}\mathrm{H}_\alpha) = 9.3$ G, 1 H; $a(^{1}\mathrm{H}_\alpha) = 6.2$ G, 1 H; $a(^{14}\mathrm{N}) = 2.0$ G, 1 N; line width, 2.6 G; sweep, 12.55 G cm^{-1}.

Scheme I



ESR spectrum of this material is a 1:1:2:2:1:1 doublet of triplets centred at $g = 1.988$ due to coupling to two phosphorus-31 nuclei ($a(^{31}\mathrm{P}) = 21.7$ G) and the hydride ($a(\mathrm{H}) = 8.7$ G). The same reaction with molecular deuterium produces the corresponding deuteride Zr(η^5-C$_5$H$_5$)D[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] (**7**-d_1). Although we have not been able to isolate this material as a solid due to its high solubility in hydrocarbon solvents, by ^{1}H NMR spectroscopy no diamagnetic products are observed, and no other paramagnetic products can be detected by ESR spectroscopy. In the absence of H$_2$, the hydride **7** is thermally stable for 48 h at room temperature, as evidenced by a lack of diminishment of the doublet of triplets ESR signal. It is reactive, however, since addition of ethylene to the paramagnetic hydride **7** immediately results in the formation of the zirconium(III) ethyl complex **8** (Scheme I). The ESR spectral and analytical data[31] of the ethyl derivative are identical to those of the compound prepared by addition of ethyllithium to the starting Zr(III) chloride **2** (Scheme I). Also noteworthy is the reaction of the deuteride **7**-d_1 with ethylene to produce the monodeuterioethyl complex Zr(η^5-C$_5$H$_5$)CH$_2$CH$_2$D[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] (**8**-d_1), in which the deuterium is only found at the β-position. Solution monitoring by ESR spectroscopy shows that over a period of 72 h, there is no scrambling of the β-deuterium into the α-position, consistent with no β-elimination for this Zr(III) alkyl derivative. In this respect, these zirconium(III) alkyls mirror related zirconocene alkyl derivatives, for which β-elimination is a slow process for unhindered alkyl derivatives.[37]

Although a number paramagnetic hydrides have been isolated and characterized,[38,39] little has been reported about their reactivity patterns. In this preliminary communication, we have shown that a Zr(III) hydride can be prepared from the corresponding Zr(III) alkyl precursors and that migratory insertion reactions of the resulting hydride can be accessed by these systems. Further studies are in progress to extend these migratory insertion reactions as well as to investigate the possibility of coupling electron transfer to hydride addition.

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Supplementary Material Available: Experimental details for the synthesis and characterization of all compounds, including ESR spectra and corresponding simulations, X-ray crystal structure analyses, and tables of bond lengths, bond angles, and atomic parameters (43 pages); listing of observed and calculated structure factors (51 pages). Ordering information is given on any current masthead page.

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